

# Allyl Stearate Copolymers and Terpolymers: Thermal, Mechanical, and Solution Properties of Polymers Incorporating Vinyl Chloride

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## Synopsis

Poly(allyl stearate) and selected copolymers and terpolymers modified by allyl stearate were investigated in this work. The systems selected and studied over a wide range of composition, included copolymers with vinyl stearate and with vinyl chloride, and terpolymers containing vinyl chloride and allyl stearate, modified further by vinyl stearate or vinyl acetate. Copolymers of allyl stearate and vinyl stearate were studied incrementally across the range of composition. In the ester copolymers the effect of degradative chain transfer on crystallization and solution properties was studied. A relation was obtained between intrinsic viscosities and number-average molecular weights; a shift in molecular weight distribution with increase in allyl component was demonstrated. The crystallinity contributed by the side chains was shown to be characterized by isomorphic replacement regardless of molecular weight. Mechanical properties of internally plasticized copolymers of allyl stearate and vinyl chloride, in a limited composition range, were compared with corresponding data for copolymers of vinyl stearate and vinyl chloride. While molecular weight reduction of the allylic copolymers exceeded that for the vinyl ester system, the effect, in the useful plasticization composition range, was not enough to grossly affect ultimate properties. The glass transitions of the hypothetical amorphous homopolymers of both fatty esters were estimated to be the same. Because this  $T_g$  was low (ca.  $-110^\circ\text{C}$ ), only relatively small mole fractions of allyl stearate were needed for effective plasticization. Isochronal temperature-composition diagrams also showed both systems to be essentially identical, but marked differences were found for diluent mixtures incorporating di-2-ethylhexyl phthalate (DOP). An empirical equation, previously derived, adequately predicted the decline in degree of polymerization with increase in allyl stearate between the limits of the respective homopolymers for all copolymers studied. Terpolymers followed the trends of the copolymers and offered no special property advantage.

## INTRODUCTION

It has long been known that allylic monomers yield copolymers having molecular weights considerably lower than those produced by copolymerization with vinyl monomers. This is the conclusion gleaned from largely qualitative studies of radical-induced copolymerizations with allylic comonomers.<sup>1-10</sup> Details of the reduction in molecular weight were treated more quantitatively, recently, for a series of vinyl comonomers polymerized

in the presence of *N*-allylstearamide.<sup>11</sup> However, this allylic comonomer is somewhat atypical in its homopolymerization and copolymerization behavior. Extreme wastage of peroxide radicals occurred from side reactions which also induced decomposition of the initiator. These reactions led to exceptionally low molecular weights and polymer yields of both homopolymers<sup>12</sup> and copolymers.<sup>11</sup> The reduction in molecular weight of copolymers was shown<sup>11</sup> to be controlled by the mole fraction of amide entering the copolymer, an effect that appeared from the work to apply generally to allylic copolymer systems. A conclusion from this publication<sup>11</sup> was that the more potentially useful, random copolymers containing allylic comonomers should have the lowest molecular weights. Because induced decomposition, leading to initiator wastage, is of less importance in the homopolymerization of allyl acetate,<sup>13</sup> allyl esters should act more favorably than allyl amides when used in copolymerization. However, maximum molecular weight reduction for the class should again occur in largely random copolymers.

Fatty comonomers, by reason of the low glass transition of their hypothetical amorphous homopolymers,<sup>14-16</sup> are more efficient as internal plasticizers than lower homologs. For flexible C<sub>17-18</sub> vinyl polyesters,  $T_g$  was estimated to be about  $-111^\circ\text{C}$ ;<sup>14</sup> for the polyamides the value was about  $-48^\circ\text{C}$ .<sup>15</sup> Consequently, small mole fractions of fatty comonomers can effect appreciable modification of stiff polymers.<sup>16</sup> This suggests that allyl stearate could be incorporated as a primary internal plasticizer, even in random copolymers, before severe reduction in both molecular weight and conversion, through degradative chain transfer,<sup>17</sup> could act to decrease useful properties. Of considerable practical importance, allyl stearate can be readily and economically prepared, without the specialized plant and large volume production required economically to manufacture vinyl stearate. There are also more fundamental reasons for studying this monomer. The crystallinity contributed by the side chains of fatty homopolymers and copolymers has recently been investigated by calorimetry at this laboratory<sup>18,19</sup> and by x-ray diffraction.<sup>20,21</sup> The effect of oligomerization on side-chain crystallinity can be gauged by the heats of fusion and the melting behavior of the present systems. For amorphous compositions, the effect of molecular weight on the glass transition may also be investigated. It has recently been demonstrated<sup>15</sup> that linear side chains act quantitatively as chain ends in reducing  $T_g$  in amorphous copolymers, in accordance with the relation

$$T_g = T_{ga} - c_p(w_b/\text{MW}_b) \quad (1)$$

where  $T_{ga}$  is the  $T_g$  of the homopolymer undergoing modification, and  $w_b$  and  $\text{MW}_b$  are the weight fraction and molecular weight, respectively, of the plasticizing comonomer having linear side chains. The proportionality constant,  $c_p$ , is in turn linearly related to the side-chain length  $n$ , in accordance with the relation

$$c_p = c_{p0} + Cn \quad (2)$$

so that there is an additive contribution to the lowering of  $T_g$  by each side-chain methylene. These relations predict that reduction in  $T_g$  would be insensitive to any but the most substantial lowering of molecular weight,<sup>22</sup> such as might be induced by degradative effects in allylic copolymerization. However, mechanical properties, which depend on a broader range of the spectrum of relaxation time,<sup>23</sup> would be affected by lowered molecular weight, perhaps severely. The present system, then, provides an excellent opportunity to test these principles.

The purpose of this investigation was to provide an extensive study of the homopolymerization and copolymerization characteristics of the monomer, allyl stearate, and of the solution, thermal, and mechanical properties of some of its copolymers. Included in the study were copolymers of allyl stearate and vinyl stearate, across the range of compositions. Here the emphasis was on copolymer molecular weights and molecular weight distributions, as well as on their heats of fusion and melting points. Also studied were copolymers of allyl stearate and vinyl chloride and terpolymers of vinyl chloride utilizing allyl stearate together with either vinyl stearate or vinyl acetate as modifiers of mechanical properties. Comparison of the mechanical properties for the vinyl chloride systems was made with reference to their molecular weights and molecular weight distributions. A background for comparison of mechanical properties with systems having higher molecular weights was provided by similarly prepared copolymers of vinyl stearate and vinyl chloride, and their vinyl acetate-containing terpolymers. Such systems were extensively studied and reported in recent publications.<sup>16,24</sup> For comparison with effects of liquid diluents, properties of poly(vinyl chloride) externally plasticized by di-2-ethylhexyl phthalate (DOP) were also provided in the published work.

## EXPERIMENTAL

### Starting Materials

Starting materials were the purest available commercially. Allyl alcohol was distilled before use through an efficient column. Stearic acid was crystallized twice from acetone (10 ml/g) to yield a product, mp 69–70°C, acid number 197.9, 99% pure by gas-liquid chromatography (as its methyl ester).

### Allyl Stearate Preparation

The stearic acid was refluxed with allyl alcohol (7 moles of alcohol per mole of acid, containing 2% of 98% sulfuric acid, based on stearic acid as catalyst,) for 4 hr and poured into an excess of hot water. The oil, washed till free of mineral acid, was air-dried, treated with activated alumina, mesh grade F-20 (1 g/g ester in 12 ml of a 50–50 mixture of petroleum ether and methylene chloride) to free it of stearic acid, and crystallized once from acetone (7.5 ml/g) at 0°C. The average yield of pure ester was 71.4%.

mp 36.0–37.0°C, acid number  $\sim 0$ , 99% pure by thin-layer chromatography.

ANAL. Calcd: C, 77.72%; H, 12.42%. Found: C, 77.83%; H, 12.47%.

### Homopolymerization of Allyl Stearate

Allyl stearate was polymerized in bulk under nitrogen with the use of 3.95 mole-% benzoyl peroxide for 48 hr. Experiment 1 was carried out at 60°C; experiment 2, at 80°C. The crude homopolymer, after precipitation in methanol at room temperature, was extracted five or six times with methanol (5 ml/g) by heating initially to 50°C for 1 hr, then cooling to 30°C. Extractions were repeated until an aliquot was no longer turbid in water and the monomer was dried as a crushed solid. This extraction procedure produced minimum homopolymer fractionation. Capillary melting points were 55–58°C for the 60°C experiment and 53–55°C for the high-temperature run.

### Copolymerization and Terpolymerization Procedure

Copolymers of allyl stearate and vinyl stearate were prepared in bulk in a nitrogen atmosphere at 60°C for 48 hr with the use of 0.5 mole-% of bisazoisobutyronitrile (AIBN) for all of the experiments. Monomer was removed by the same procedure used for the homopolymers. The procedure of Jordan et al.<sup>16</sup> was followed for the vinyl chloride copolymers and terpolymers, except that 0.25 mole-% of AIBN was used as initiator and petroleum ether was used instead of methanol to extract the monomers in experiments 44, 45, 49–52.

### Molecular Weights and Molecular Weight Distributions

Number-average molecular weights were obtained by reported procedures;<sup>25</sup> the densest membranes manufactured by Schleicher and Schuell for use with the instrument (type 0–8) were used with toluene. Readings were taken immediately after equilibrium was reached; extrapolation to zero time produced no difference in  $\bar{M}_n$ . Permeation did occur to a small, but undetermined, extent in the systems rich in allyl stearate, as evidenced by a slow drift to lower pressures.

Gel-permeation chromatography (GPC) was performed on selected samples by Waters Associates, Framingham, Mass. Analytical conditions were as described below. For the homopolymers, an eight-column styrogel set was used, having polystyrene contour length exclusion values, in pairs, of, respectively,  $1 \times 10^3$  Å, 500 Å, 100 Å, and 60 Å. The solvent, tetrahydrofuran (THF), was maintained at a flow rate of 2 ml/min at 22°C. For the allyl and vinyl stearate copolymers, five columns were packed with a styrogel mix of polystyrene having contour chain-length exclusion values of, for the first two columns,  $1 \times 10^6$  Å,  $1 \times 10^5$  Å,  $1 \times 10^4$  Å, and  $1 \times 10^3$  Å; for the next two columns,  $1 \times 10^4$  Å,  $1 \times 10^3$  Å, 600 Å, and 240 Å; for the last column, 600 Å, 240 Å, 100 Å, and 60 Å. The solvent, THF, was

maintained at a flow rate of 1.5 ml/min at 22°C. For the vinyl chloride copolymers and terpolymers, five columns were packed with a styrogel of polystyrene contour chain length exclusion limits of  $1 \times 10^6$  Å,  $1 \times 10^5$  Å,  $7 \times 10^3$  Å,  $1 \times 10^3$  Å, and 500 Å, respectively. The flow rate of THF was 2 ml/min. Elution volumes for the homopolymers were correlated with monodisperse polystyrene, poly(propylene glycol), and hydrocarbon solvents, and against monodisperse polystyrene fractions for the rest. Molecular weights and degrees of polymerization for the unknowns of this study were estimated by computer analysis of the individual scans, using molecular weights of the polystyrene standards to construct a calibration curve. This procedure cannot give accurate results. When a universal calibration procedure is not available,<sup>26</sup> accurate results can be provided only by using monodisperse fractions of the material under investigation as standards.<sup>27</sup> Consequently, the distributions reported below, while accurate on a relative basis, are only approximate as absolute values; they are only intended to give the reader a clearer picture of the magnitude of the change in degrees of polymerization than can be obtained using the less descriptive contour length designation. However, perhaps by fortuitous circumstance, molecular weight averages by both osmometry and GPC were generally close. Intrinsic viscosities in benzene at 30°C were obtained by purchase order from Arrow Laboratories.

### Other Properties

Mechanical properties and specimen preparation followed reported procedures.<sup>16,25</sup> Thermodynamic data were obtained by differential scanning calorimetry by reported procedures,<sup>14,18,19</sup> as were the refractometric melting points. Calculations and correlations were generally done by using an IBM 1130 computer.

## RESULTS AND DISCUSSION

### General Features

The feed and polymer compositions, per cent conversions, molecular weights, and degrees of polymerization are listed in Table I. The various systems studied are grouped and titled in the table. Study of the allyl stearate-vinyl stearate copolymers focused on effects of side-chain crystallinity, per cent conversion, and molecular weights and their distribution. Side-chain crystallization and molecular weight reduction for this system will be treated more fully in the sections below. The way in which mechanical properties were affected by progressively declining molecular weight, as the allyl stearate content increased, was stressed for the remaining systems in the table.

Specific mechanical properties are shown in Table II and will be discussed below. For comparison with internally plasticized compositions having smaller reductions in conversions and molecular weights, data for copoly-

TABLE I  
Feed and Polymer Compositions, Conversions, and Molecular Weights

Expt. no.	Feed composition, mole fraction		Polymer composition, mole fraction			$w_b$ feed <sup>b</sup>	Conver- sion, %	Molecular weights			
	$m_{AS}$	$m_{VE}^a$	$m_{VCl}$	$m_{AS}$	$m_{VE}^a$			$\bar{M}_n^c$	$\bar{X}_n^d$	$[\eta]$	
Homopolymers: poly(allyl stearate)											
1	1.00			1.00		1.00	34.0	10,900	33.7	0.053	
2	1.00			1.00		1.00	74.2	11,000	34.2	0.053	
Copolymers: allyl stearate and vinyl stearate											
3	0	1.00		0	1.00	0	98.3	75,100	242	0.311	
4	0.10	0.90		0.10	0.90	0.104	96.8	70,700	227	0.270	
5	0.20	0.80		0.20	0.80	0.206	76.5	45,700	146		
6	0.30	0.70		0.30	0.70	0.308	53.7	32,900	104	0.128	
7	0.40	0.60		0.40	0.60	0.410	37.7	27,600	87.3		
8	0.50	0.50		0.50	0.50	0.510	25.7	22,600	71.0	0.096	
9	0.60	0.40		0.60	0.40	0.611	18.9	20,900	65.4		
10	0.70	0.30		0.70	0.30	0.710	13.6	17,700	55.1	0.086	
11	0.80	0.20		0.80	0.20	0.808	9.9	15,500	48.0		
12	0.90	0.10		0.90	0.10	0.902	6.7	13,400	41.3	0.060	

Copolymers: allyl stearate and vinyl chloride <sup>a</sup>									
13	0	1.00	0	1.00	0	88.9	—	—	—
14	0.024	0.976	0.0234	0.977	0.113	89.8	87,700	1280	
15	0.048	0.952	0.0483	0.952	0.207	89.7	71,800	955	
16	0.072	0.928	0.0720	0.928	0.287	88.1	52,800	649	
17	0.096	0.904	0.0828	0.917	0.356	80.9	39,100	464	
18	0.144	0.856	0.115	0.885	0.467	64.1	27,700	299	
19	0.193	0.807	0.146	0.854	0.554	51.9	23,800	236	
20	0.242	0.758	0.187	0.813	0.624	38.3	20,300	182	
21	0.278	0.722	0.210	0.790	0.646	36.8	19,300	164	
Copolymers: vinyl stearate and vinyl chloride <sup>a</sup>									
22	0.025	0.975	0.027	0.974	0.113	93.7	—	—	—
23	0.050	0.950	0.055	0.942	0.207	96.4	61,600	823	
24	0.075	0.925	0.075	0.925	0.287	94.6	60,100	745	
25	0.100	0.900	0.097	0.903	0.356	95.6	57,700	663	
26	0.150	0.850	0.144	0.856	0.467	91.5	59,100	594	
27	0.200	0.800	0.193	0.807	0.554	93.0	59,400	529	
28	0.250	0.750	0.250	0.750	0.624	85.7	60,700	487	
29	0.287	0.713	0.280	0.720	0.641	78.0	57,800	441	
Terpolymers: allyl stearate, vinyl stearate and vinyl chloride <sup>d</sup>									
30	0.024	0.976	0.024	0.976	0.113	92.5	88,900	1292	
31	0.048	0.952	0.047	0.953	0.207	90.0	67,400	901	
32	0.052	0.927	0.053	0.926	0.287	93.7	53,800	660	
33	0.056	0.902	0.052	0.908	0.356	86.7	41,600	484	
34	0.064	0.853	0.052	0.877	0.467	82.2	35,400	379	
35	0.071	0.803	0.059	0.836	0.554	75.2	33,200	319	
36	0.080	0.753	0.070	0.783	0.624	69.1	31,350	267	
37	0.089	0.716	0.088	0.720	0.641	55.3	27,600	207	

TABLE I (continued)

Expt. no.	Feed composition, mole fraction			Polymer composition, mole fraction			$w_b$ feed <sup>b</sup>	Conver- sion, %	Molecular weights	
	$m_{AS}$	$m_{VE}^a$	$m_{VCl}$	$m_{AS}$	$m_{VE}^a$	$m_{VCl}$			$\bar{M}_n^c$	$\bar{X}_n^d$ [ $\eta$ ]
Terpolymers: allyl stearate, vinyl acetate and vinyl chloride <sup>f</sup>										
38	0	0.400	0.600	0	0.344	0.656	0.419	92.8	43,000	508
39	0.025	0.375	"	0.024	0.356	0.620	0.519	88.7	57,700	748
40	0.050	0.350	"	0.046	0.322	0.632	0.553	85.4	41,300	503
41	0.100	0.300	"	0.078	0.233	0.689	0.608	73.5	28,350	321
42	0.150	0.250	"	0.110	0.184	0.706	0.652	55.0	23,850	249
43	0	0.600	0.400	0	0.588	0.412	0.663	98.9	74,900	977
44	0.025	0.575	"	0.024	0.557	0.419	0.697	97.1	62,000	756
45	0.050	0.550	"	0.048	0.522	0.430	0.718	89.5	45,700	524
46	0.100	0.500	"	0.083	0.415	0.502	0.751	66.5	37,400	398
47	0.150	0.450	"	0.115	0.344	0.541	0.778	45.7	28,500	283
48	0	0.800	0.200	0	0.776	0.224	0.827	98.9	115,000	1410
49	0.025	0.775	"	0.025	0.763	0.213	0.857	96.8	109,000	1249
50	0.050	0.750	"	0.048	0.714	0.239	0.867	83.0	66,000	719
51	0.100	0.700	"	0.088	0.618	0.294	0.881	68.0	50,300	501
52	0.150	0.650	"	0.121	0.518	0.362	0.888	23.9	45,300	426

<sup>a</sup> Mole fraction of vinyl stearate, expts. 3-12 and 32-37; mole fraction of vinyl acetate, expts. 38-52.

<sup>b</sup>  $w_b = w_{AS} + w_{VE}$ .

<sup>c</sup> Determined by membrane osmometry. Consequently these values tend to be high, especially at high allyl stearate contents.

<sup>d</sup> Computed by using  $\bar{M}_n/[m_{AS}MW_{AS} + m_{VE}MW_{VE} + m_{VCl}MW_{VCl}]$ , where MW is the molecular weight of the monomer and the subscripts AS, VE, VCl are, respectively allyl stearate, vinyl ester, (vinyl stearate or vinyl acetate) and vinyl chloride. Found mole fractions from percent Cl analyses used.

<sup>e</sup> Polymer composition from per cent Cl determinations. In the allyl stearate-vinyl chloride copolymers, the mole fraction of allyl stearate from per cent C determinations were, expt. number; mole fraction: 14, 0.0212; 15, 0.0466; 16, 0.0702; 17, 0.0996; 18, 0.119; 19, 0.154; 20, 0.194; 21, 0.230.

<sup>f</sup> Calculated by using assumptions and methods reported elsewhere.<sup>16, 28</sup>



mers of vinyl stearate and vinyl chloride, taken from other studies from this laboratory<sup>16,24</sup> are included in Table I. The two vinyl chloride copolymer systems had the same feed weight fractions  $w_b$ . Two types of terpolymers were studied. For the terpolymers containing vinyl stearate, the weight fraction of allyl stearate was held constant (at 0.21), while vinyl stearate was incrementally increased at the expense of vinyl chloride. Thus the degradative effect of allyl stearate was maintained at a constant low level, while plasticization was increased with vinyl stearate. In the remaining terpolymers, vinyl acetate was incrementally replaced by allyl stearate from copolymers of vinyl acetate and vinyl chloride, at three vinyl chloride feed compositions. These also parallel studies of vinyl acetate-containing terpolymers incorporating vinyl stearate.<sup>16,24</sup> Because of possible and unpredictable drift in composition with conversion, both feed and polymer compositions are listed in Table I. Compositions of the vinyl chloride copolymers were calculated from elemental analyses for chlorine; compositions by per cent carbon agreed closely. Compositions of the terpolymers were obtained from elemental chlorine and carbon analyses, following procedures and assumptions previously reported.<sup>16,28</sup>

Monomer reactivity ratios for allyl stearate and vinyl chloride copolymers having relatively low conversions (experiments 18–21) were calculated by the procedure of Fineman and Ross<sup>29</sup> from both elemental chlorine and carbon. Ratios by the two methods were similar; average values and their copolymerization parameters were ( $M_1$ , vinyl chloride):  $r_1 = 1.27$ ,  $r_2 = 0.52$ ;  $Q_2 = 0.0304$ ,  $e_2 = -0.44$ . These agree closely with literature values<sup>30a</sup> for vinyl stearate and other vinyl and allyl esters. Consequently, the segmental distribution of both plasticizing comonomers should be nearly identical for the same feed compositions at similar conversions. It is not surprising, therefore, that feed and found composition of the allyl and vinyl stearate copolymers, at low conversion, were the same within the experimental error of estimation. Monomers having identical reactivity have ratios,  $r_1 = r_2 = 1$ .<sup>31,32</sup> Because of possible drift in composition with conversion, for the vinyl chloride systems, all correlations are made in this paper against found composition.

Table II lists glass transition temperatures, mechanical properties, melting points, and heats of fusion obtained for the systems investigated. The table is sectioned, as was Table I, and the experimental numbers of both coincide. Trends of both glass transitions and mechanical properties were similar to those found for other internally plasticized copolymers<sup>14–16</sup> and terpolymers.<sup>16,24,28</sup> Both types of property declined to a weight fraction of long side-chain ester of about 0.3 to 0.5, then rose as side-chain crystallization developed ( $\Delta H_f$ ). The ultimate properties of the allyl ester copolymers were somewhat lower than those of the copolymers plasticized by vinyl stearate. The former undoubtedly reflect the influence of lesser chain entanglement as expected for lower molecular weight polymers.<sup>23</sup> In the sections below, the influence of allyl stearate content on molecular weights, glass transitions, mechanical properties, and side-chain crystallinity will be correlated and discussed in greater detail.

TABLE II  
Glass Transition Temperatures, Mechanical Properties, Melting Points, and Heats of Fusion for the Copolymers and Terpolymers

Polymer composition, wt fraction			Mechanical properties <sup>a</sup>					Side-chain crystallinity		
Expt. no.	w <sub>AS</sub>	w <sub>b</sub>	T <sub>g</sub> , °C	$\bar{E}_t \times 10^{-5}$ , psi	FS, psi	E <sub>t</sub> × 10 <sup>-5</sup> , psi <sup>b</sup>	TS, psi	Elongation, %	T <sub>m</sub> , °C	ΔH <sub>f</sub> , cal/g
Homopolymers: poly(allyl stearate)										
1	1.00		18.0						59.0	23.7
2	"		"						55.0	22.4
Copolymers: allyl stearate and vinyl stearate										
Mechanical properties not determined for this series										
3	0	0	17.9						54.5	20.3
4	0.104	0.104	"						54.0 <sup>c</sup>	21.3
5	0.206	0.206	"						55.0	21.3
6	0.308	0.308	"						56.0 <sup>c</sup>	22.4
7	0.410	0.410	"						57.0 <sup>c</sup>	22.7
8	0.510	0.510	"						58.0	22.1
9	0.611	0.611	"						58.0 <sup>c</sup>	22.4
10	0.710	0.710	"						58.7 <sup>c</sup>	22.6
11	0.808	0.808	"						59.0	22.9
12	0.902	0.902	"						59.0	22.9
Copolymers: allyl stearate and vinyl chloride										
13	0	0	81.0	2.26	5210	1.90	6270	4.1		
14	0.111	0.111	57.0	1.64	3680	2.17	5840	9.2		
15	0.209	0.209	32.0	0.717	1560	1.24	5060	15.3		
16	0.287	0.287	24.0	0.047	98	0.125	1860	124		
17	0.319	0.319	16.9	0.018	41	0.076	1460	98.3		
18	0.402	0.402	4.9	0.004	10	0.027	674	307		
19	0.469	0.469	20.0	0.022	47	0.029	331	163	34.0 <sup>d</sup>	1.2
20	0.544	0.544	20.9	0.098	194	0.177	840	20.0	37.0 <sup>d</sup>	4.3
21	0.579	0.579	22.8	0.147	282	0.291	734	13.5	38.0 <sup>d</sup>	5.9

Copolymers: vinyl stearate and vinyl chloride<sup>a</sup>

22	0.119	0.119	59.0	1.93	4300	1.68	6430	6.8
23	0.225	0.225	41.0	1.14	2450	1.50	5830	11.4
24	0.286	0.286	25.0	0.593	1320	1.02	3120	34.6
25	0.348	0.348	13.0	0.072	172	0.153	2280	117
26	0.455	0.455	1.9	0.008	21	0.008	1180	155
27	0.543	0.543	17.0	0.027	65	0.009	981	207
28	0.623	0.623	18.9	0.128	277	0.010	976	66.5
29	0.659	0.659	19.0	0.192	401	0.268	1730	5.0

40.0<sup>d</sup>  
42.0<sup>d</sup>  
46.0<sup>d</sup>  
47.0<sup>d</sup>

0.5  
1.7  
5.2  
6.6

Terpolymers: allyl stearate, vinyl stearate, and vinyl chloride

30	0.113	0.113	57.0	1.55	3140	1.70	4340	7.1
31	0.204	0.204	27.0	0.713	1580	1.17	3530	29.3
32	0.209	0.290	24.0	0.055	139	0.082	2000	45.8
33	0.198	0.340	18.0	0.030	74	0.080	1740	70.5
34	0.184	0.416	8.9	0.003	10	0.006	1460	110
35	0.186	0.498	17.0	0.018	37	0.006	552	270
36	0.193	0.583	7.0	0.095	192	0.049	796	19.3
37	0.214	0.662	17.9	0.193	391	0.294	968	7.3

36.0<sup>d</sup>  
38.0<sup>d</sup>  
41.0<sup>d</sup>

1.7  
4.2  
8.4

TABLE II (continued)

TABLE II (continued)									
Polymer composition, wt fraction			$T_g$ , °C	Mechanical properties <sup>a</sup>				Side-chain crystallinity	
Expt. no.	$w_{AS}$	$w_b$		$E_t \times 10^{-5}$ , psi	FS, psi	$E_t \times 10^{-5}$ , psi <sup>b</sup>	TS, psi	Elongation, %	$T_m$ , °C
Terpolymers: allyl stearate, vinyl acetate, and vinyl chloride									
38	0	0.419	55.0	2.25	4840	2.28	6030	4.0	
39	0.099	0.498	39.0	1.80	3850	1.85	7920	4.0	
40	0.182	0.519	24.0	0.859	1870	1.36	5340	15.0	
41	0.286	0.513	0.90 <sup>f</sup>	0.040	85	0.098	1260	93.0	
42	0.374	0.539	9.90 <sup>f</sup>	0.049	110	0.022	671	30.0	
43	0	0.663	21.0	1.38	3210	1.92	5200	9.9	39.9 <sup>d</sup>
44	0.096	0.680	37.0	0.146	333	0.047	2010	66.0	
45	0.178	0.692	26.0	0.126	371	0.018	1700	111	
46	0.286	0.666	14.0 <sup>f</sup>	0.039	85	0.012	1180	101	
47	0.370	0.664	12.0 <sup>f</sup>	0.060	134	0.036	613	33.0	
48	0	0.827	23.9	0.137	350	0.517	1860	14.0	43.0 <sup>d</sup>
49	0.092	0.847	20.9	0.070	149	0.012	1190	204	
50	0.168	0.838	12.0 <sup>f</sup>	0.221	451	0.103	2190	58.0	
51	0.286	0.817	15.0 <sup>f</sup>	0.067	155	0.047	793	15.0	
52	0.368	0.787	14.0 <sup>f</sup>	0.140	307	0.020	126	7.5	37.0 <sup>d</sup>
Designations are: $E_t$ , flexural modulus; FS, flexural strength; TS, tensile strength; $T_g$ , glass transition temperature; $T_m$ , melting point; $\Delta H_t$ , heat of fusion.									0.65

<sup>a</sup> Designations are:  $E_t$ , flexural modulus; FS, flexural strength;  $E_t$ , tensile modulus; TS, tensile strength.

<sup>b</sup> Secant modulus. Where % elongations exceeded 100%, the 100% modulus is given.

<sup>c</sup> Capillary melting points; the rest are refractometric.

<sup>d</sup> Determined by differential scanning calorimetry.

<sup>e</sup> Data from reference 16.

<sup>f</sup> Two  $T_g$ 's found. Higher values were, in this order, experiment number,  $T_g$ : 41, 75; 42, 72; 46, 57; 47, 62; 50, 54; 51, 47; 52, 47.

### Effect of Allyl Stearate Content on Molecular Weight and Degree of Polymerization

Number-average molecular weights for all polymers in Table I were obtained by membrane osmometry. Because of the well-known permeation of small species through membranes,<sup>33,34</sup> apparent molecular weights and degrees of polymerization for the homopolymer and compositions rich in allyl stearate are undoubtedly high. Degrees of polymerization ( $\bar{X}_n$ ) for poly(allyl acetate) were reported to be around 15–25;<sup>13,17</sup> because effective chain transfer for allyl stearate would be greater than for vinyl acetate,<sup>35</sup>  $\bar{X}_n$  should be less than these values. A value of around 7 was, in fact, reported for allyl laurate.<sup>35</sup> It is of interest that an estimate of  $\bar{X}_n$  of 8.1 was obtained as an average by gel-permeation chromatography for poly(allyl stearate) (experiment 1) by using the oligomeric standards described in the experimental section. The osmometric value (Table I) is much higher. On the other hand, the adventitious presence of monomer and other low species would severely reduce  $\bar{X}_n$  by GPC.

Intrinsic viscosities  $[\eta]$  in benzene at 30°C and number-average molecular weights  $\bar{M}_n$  are listed in Table I for copolymers of allyl stearate and vinyl stearate. A decline in both  $[\eta]$  and  $\bar{M}_n$  would be expected to be a function of the concentration of the allyl ester because of the susceptibility of the allyl group to degradative chain transfer. The homopolymers of both of these monomers terminate largely by transfer to monomer,<sup>36</sup> and their reactivity ratios are close to unity, as was discussed above. Consequently, the relation between the mole fraction of allyl stearate in the copolymers might be expected to be close to a linear logarithmic function of both  $[\eta]$  and  $\bar{M}_n$ ; that is,

$$1/\bar{X}_n = \exp\{m_{AS}C_{M(AS)} + m_{VS}C_{M(VS)}\} \quad (3)$$

where  $m_i$  is the mole fraction and  $C_M$  the monomer transfer constants for units of allyl stearate (AS) and vinyl stearate (VS), respectively. In more typical copolymer systems involving allylic comonomers, reactivity ratios other than unity prevail, and the rate-dependent expression,  $(k_i/k_p^2)R_p/[M]^2$  dominates over  $C_M$  at high concentration of the nonallylic comonomer. In these systems the relation should tend to curve and hence not obey eq. (3). It was observed that the relations between  $\ln [\eta]$  and  $\ln \bar{M}_n$  and the mole fraction of allyl stearate for the all fatty copolymers were indeed linear, and followed by equations

$$\ln [\eta] = \ln [\eta]_0 - \alpha m_{AS} \quad (4)$$

$$\ln \bar{M}_n = \ln \bar{M}_{n0} - \beta m_{AS} \quad (5)$$

where  $\alpha$  and  $\beta$  are proportionality constants and  $[\eta]$  and  $\bar{M}_{n0}$  the intercepts of the respective relations. The parameters are listed in Table III. Strictly speaking, the linearity expressed by eqs. (4) and (5) should apply only at low conversions, where the most probable distributions of molecular weights are found in systems terminating by transfer.<sup>37</sup> As conversion

TABLE III  
Parameters for the Various Equations

Equation	System	Intercept	Coefficient 1	Coefficient 2	$\alpha/\beta$
4	AS + VS	-1.29	$\pm 0.11$	1.73	$\pm 0.18$
5	AS + VS	11.2	$\pm 0.1$	1.95	$\pm 0.16$
10, $F_2$	AS + VS	0.00395	$\pm 0.0006$	0.0127	$\pm 0.0029$
"	AS + VCI	0.00010	$\pm 0.00008$	0.0278	$\pm 0.0006$
"	VS + VCI	0.00103	$\pm 0.00006$	0.0049	$\pm 0.0004$
10, $m_i$	AS + VS	0.00395	$\pm 0.0006$	0.0127	$\pm 0.0029$
"	AS + VCI	0.00029	$\pm 0.00017$	0.0306	$\pm 0.0013$
"	VS + VCI	0.00102	$\pm 0.00005$	0.0044	$\pm 0.0003$
				0.0117	$\pm 0.0028$
				0.0117	$\pm 0.0028$
					0.887

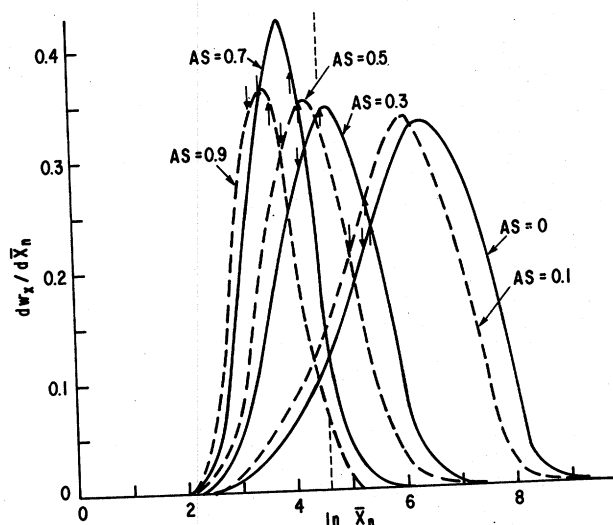


Fig. 1. Approximate differential distribution curves, plotted against the log of the degrees of polymerization,  $\ln \bar{X}_n$ , for copolymers of allyl stearate and vinyl stearate. The data are from gel-permeation chromatography (GPC). Arrows denote the number-average degree of polymerization. Arrows moving down are by GPC; arrows moving up are by membrane osmometry. Curves are labeled as the mole fraction of allyl stearate in the copolymers. Dotted line denotes  $\bar{X}_n = 100$ .

increases, transfer to polymer and increase in initiator concentration should produce a long tail into the low molecular weight end of the distribution, thus lowering average values. Conversions for the copolymers of allyl and vinyl stearate decreased steadily down the list in Table I as the allyl stearate content increased. Differential molecular weight distribution curves, obtained as estimates from GPC are shown in Figure 1. These were essentially log normal curves at high allyl stearate contents, where conversions were low (curves at the left of the figure), but developed a long tail into the low molecular weight region as the vinyl stearate content, and hence the conversion, increased (distributions to the right in the figure). Consequently, the linearity expressed by eqs. (4) and (5) may have been produced by a fortuitous reduction in molecular weight resulting from the increase in conversion. It is of interest that the average degrees of polymerization found by membrane osmometry lay close to those by GPC (positions of the arrows in the figure). Again, this may only be accidental because both methods of molecular weight estimation are subject to significant errors.

Division of eq. (4) by eq. (5) and rearrangement leads to

$$\ln[\eta] - \ln[\eta]^0 / \ln \bar{M}_n - \ln \bar{M}_{n0} = \alpha/\beta = a \quad (6)$$

Consequently, the logarithm of the intrinsic viscosity is linearly related to the logarithm of the number-average molecular weight for copolymers of

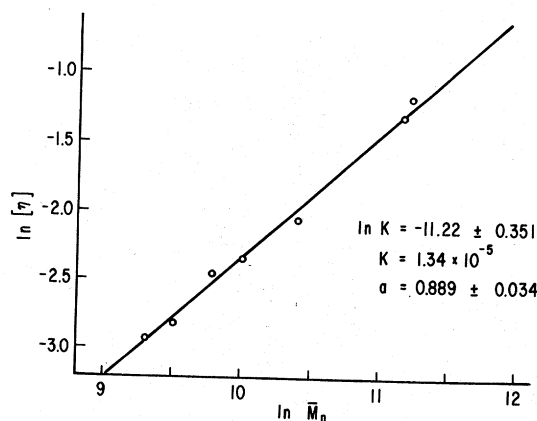


Fig. 2. Relation between intrinsic viscosity  $[\eta]$  and number-average molecular weight  $\bar{M}_n$ , for copolymers of allyl stearate and vinyl stearate. Allyl stearate content increases from right to left in accordance with the compositions listed in Table I.

allyl stearate with vinyl comonomers having the same reactivity in copolymerization. The relation is

$$[\eta] = K\bar{M}_n^a \quad (7)$$

where  $a$  is from eq. (6) and  $K$  is the constant of integration. This relationship is illustrated in Figure 2. Values of  $K$  and  $a$  are given in the figure. The value of  $a$  is close to the ratio  $\alpha/\beta$ , listed in Table III, as required. Equation (7) has the same form as the Mark-Houwink equation relating intrinsic viscosity and molecular weight of homopolymer fractions. The similar chemistry of the two comonomers suggests similar solubility parameters toward benzene. In support of this, the magnitude of  $a$  and  $K$  are close to values usually found for homopolymers in good solvents,<sup>30b</sup> although the magnitude of  $a$  seems to be a little high. Large values of  $a$  would be produced if the osmometric values for  $\bar{M}_n$  of allyl stearate-rich copolymers were a little high. It is pertinent that a value of  $a$  of 0.64 was found<sup>38</sup> for poly(*n*-octadecyl acrylate) in benzene at 30°C. It may be concluded that the presence of allyl stearate in these copolymers produced species of similar chemistry having identical affinities for benzene and differing only in molecular length. This tended to be true even as conversion increased with increase in vinyl stearate, although at high conversions, a broadening of molecular weight did occur, producing lowered average molecular weights.

The relationship just discussed between molecular weight and composition represents a limiting special case for allylic systems in that both  $r_1$  and  $r_2$  were close to unity. In a previous publication<sup>11</sup> an empirical equation was derived for the general case where  $r_1 \neq r_2$ . The expression was

$$1/\bar{X}_n = 1/\bar{X}_{n1} + K_1F_2 + K_2(F_2)^3 \quad (8)$$

where  $K_1$  is the slope at  $1/\bar{X}_1$  and  $K_2 = [(1/\bar{X}_{n2}) - (1/\bar{X}_{n1})] - K_1$ . The quantities  $1/\bar{X}_{n2}$  and  $1/\bar{X}_{n1}$  are the reciprocal number-average degrees of



polymerization of the allylic homopolymer and the vinyl homopolymer, respectively. In using eq. (8) these quantities must be experimentally ascertained, as must be the slope  $K_1$ .<sup>11</sup> In cases where the predominant mode of termination of the vinyl monomers is by chain transfer,  $C_M$  may be used as  $1/\bar{X}_{n1}$ . The variable  $F_2$  is the instant mole fraction of allyl comonomer in the copolymer and is, therefore, related to the copolymerization equation by

$$F_2 = 1 - F_1 = 1 - [(r_1 f_1^2 + f_1 f_2)/(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)] \quad (9)$$

where  $F_1$  is the instant mole fraction of the vinyl comonomer in the copolymer and  $f_i$  are feed mole fractions. Thus, the more general eq. (8), like eqs. (4) and (5), depends on the residence time of the terminal allylic group in determining the copolymer molecular weight. When the drift in composition with conversion is small,  $F_2$  will approximately equal the mole fraction  $m_b$  of allyl or vinyl stearate (Table I) in the copolymer. Data for  $1/\bar{X}_n$  for experiments 1-29 in Table I were curve-fitted by computer in accordance with the expression

$$1/\bar{X}_n = 1/\bar{X}_{n0} + AF_2 + BF_2^2 + \dots \quad (10)$$

The reactivity ratios given earlier were used, through eq. (9), to compute  $F_2$ . A second-degree polynomial was found to be significant; parameters are given in Table III. Parameters for the relation between  $1/\bar{X}_n$  and  $m_b$  by use of eq. (10), also given in Table III, are close, indicating little drift in composition with conversion. Data fitted by eqs. (8) and (10) are compared in Figure 3 with  $K_1$  taken as  $A$  (Table III) and  $1/\bar{X}_{n2}$  from experiment 1 of Table I. The quantity  $1/\bar{X}_{n1}$  for poly(vinyl chloride) was estimated as 0.000621 by extrapolation of molecular weights of experiments 14-20 to

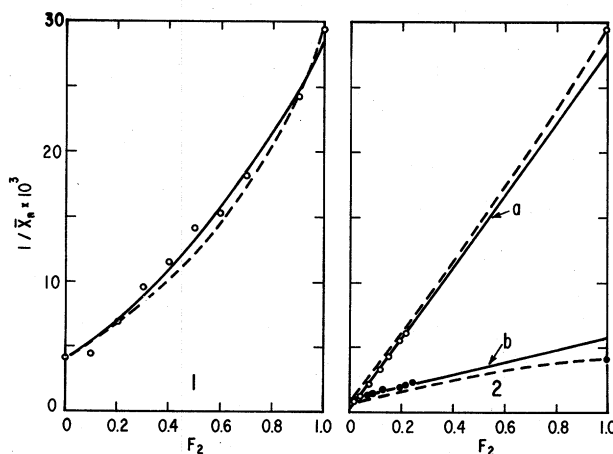


Fig. 3. Plot of  $1/\bar{X}_n$  versus the mole fraction of allyl stearate in the instant copolymer,  $F_2$ : (1) copolymers of allyl stearate and vinyl stearate; (2a) copolymers of allyl stearate and vinyl chloride; (2b) copolymers of vinyl stearate and vinyl chloride; (—) obtained by using eq. (10); (---) obtained by using eq. (8).

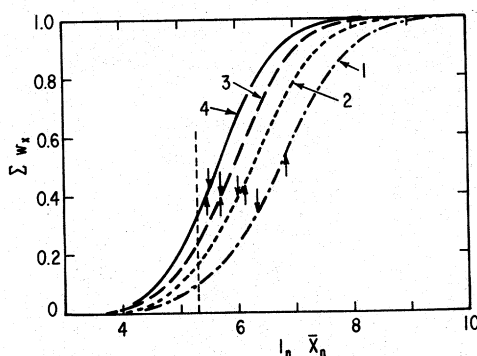


Fig. 4. Plot of the cumulative weight fraction of molecular species versus the number-average degree of polymerization,  $\bar{X}_n$ , for several copolymers of allyl stearate and vinyl chloride. Fractionation data are from gel-permeation chromatography (GPC). Numbers correspond to mole fractions of allyl stearate in the copolymer of, respectively: (1) 0.048; (2) 0.083; (3) 0.115; (4) 0.146. Arrows indicate average  $\bar{X}_n$  for the whole polymer. Arrows moving down are by GPC; those moving up are by membrane osmometry. Fractions to the left of the dotted line had degrees of polymerization less than 200.

$m_{AS} = 0$ . Agreement between the two relations is reasonably good, thus supporting the generality of eq. (8).<sup>11</sup> This equation is convenient when  $1/\bar{X}_{n1}$  and  $1/\bar{X}_{n2}$  are known, because  $K_1$  can be estimated by a single molecular weight for a copolymer poor in the allylic comonomer. While the contrast between the allyl stearate and vinyl stearate copolymers is marked (insert 2, Fig. 3), the difference in  $\bar{X}_n$  in the useful range of composition is relatively small (compare, also, data in Tables I and II).

Cumulative distribution curves from GPC are shown in Figure 4 for selected copolymers of allyl stearate and vinyl chloride. The abscissa is in degrees of polymerization. As was discussed above, these curves are only approximate. The curves were shifted to lower degrees of polymerization as the allyl stearate content increased; however, most of the distribution for all four systems lay above  $\bar{X}_n$  of 200, indicating that a significant fraction of these copolymers were in the high polymer range. Typical vinyl stearate-vinyl chloride copolymers would be expected to lie slightly to the right of curve 1. From the proximity of the arrows in the figure, the average  $\bar{X}_n$  by both GPC and osmometry are seen to be similar. It may be concluded that, while molecular weights declined steadily as allyl stearate increased, simple relationships derived from classical kinetic and solution property theory were able to describe the observed trends. Most of the range of vinyl chloride copolymers with allyl stearate had molecular weight distributions in the high polymer range.

### Correlation of the Glass Transition Temperature with Composition

A general empirical equation for the change in glass transition of a two component system with weight fraction  $w_i$  of plasticizer, including internal plasticizers,<sup>39,40</sup> is

$$T_g = w_a T_{ga} + w_b T_{gb} + K w_a w_b \quad (11)$$

where the subscripts (a and b) designate the  $T_g$  for the respective homopolymers and  $K$  is an empirical constant. In special cases, where  $K = 0$ , eq. (1) becomes

$$T_g = w_a T_{ga} + w_b T_{gb} \quad (12)$$

The linear equation can be expressed as

$$T_g = T_{ga} - k w_b \quad (13)$$

under conditions that  $T_{ga} > T_{gb}$  so that  $k$  is equal to  $T_{ga} - T_{gb}$ . Equation (11) applies to many externally plasticized systems,<sup>39,40</sup> while eq. (13) often describes copolymers containing internal plasticizers having long linear side chains.<sup>14-16,24,28</sup> Equation (13) was used to calculate the dashed

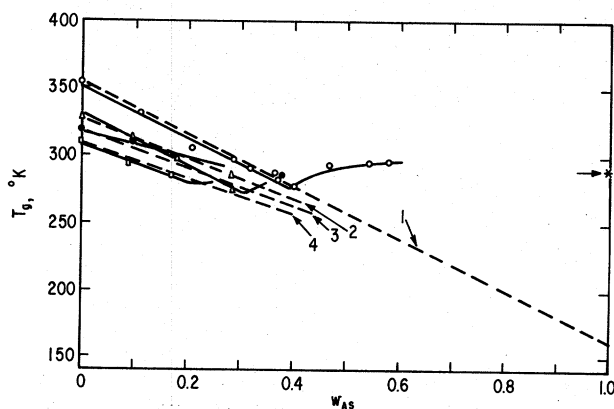


Fig. 5. Plot of the glass transition temperature  $T_g$  vs. the weight fraction of allyl stearate  $w_{AS}$  in the copolymers and terpolymers: (---) theoretical, calculated by using eqs. (12) and (14); (—) curve fitted by using the computer and experimental data; (1) copolymers of allyl stearate and vinyl chloride; (2, 3, 4) terpolymers of allyl stearate, vinyl acetate, and vinyl chloride, in which the mole fraction of vinyl chloride in the feed was, respectively, 0.60, 0.40, and 0.20.

line (line 1) in Figure 5 for amorphous copolymers of allyl stearate and vinyl chloride.  $T_{ga}$  was taken as 354°K<sup>16</sup> and  $T_{gb}$  as 162°K.<sup>14</sup> The corresponding solid line in the figure represents a computer fit of the experimental data. The solid and dashed lines nearly coincide up to  $w_{AS}$  of 0.4, indicating that the hypothetical amorphous homopolymer, poly(allyl stearate), also has, on extrapolation, a  $T_g$  near the value of 162°K (−111°C) found for other flexible poly(vinyl esters).<sup>14,16</sup> Consequently, allyl stearate appears to be as efficient an internal plasticizer as vinyl stearate. Insensitivity of the  $T_g$  decline to moderate reduction in main-chain length, predicted by eqs. (1) and (2), and discussed in the introduction, also seems supported by the data available.

For terpolymers, like the vinyl acetate systems being considered in this paper (experiments 38–52), where two homologs act additively to plasticize a third component, eq. (12) may be modified to yield

$$T_g = w_a T_{ga} + w_{AS} T_{gAS} + w_{VA} T_{gVA} \quad (14)$$

where the subscripts AS and VA are allyl stearate and vinyl acetate, respectively. Equation (14) was used to calculate the dashed lines 2, 3, 4 for the terpolymers in Figure 5 with  $T_{ga}$  taken as 354°K<sup>16</sup>  $T_{gAS}$  as 162°K, [same as  $T_{gb}$  of eq. (13)] and  $T_{gVA}$  as 301°K.<sup>30c</sup> Agreement between calculated and experimental values is only fair, as can be seen. The data for the terpolymers was complicated by the appearance of a second and higher  $T_g$  in the terpolymer systems rich in allyl stearate (Table II). While some compositional heterogeneity was undoubtedly present in these systems,<sup>41</sup> it was not reflected as a bimodal distribution in molecular-weight analysis by GPC. Therefore, the aggregates of the molecular species responsible for a double  $T_g$  were not appreciably rich in either allyl stearate or vinyl chloride. The upward movement of the experimental data beyond  $w_{AS}$  of 0.3–0.4 reflected the usual influence of developing side-chain crystallinity (Table II) on  $T_g$ .<sup>14–16, 24, 28</sup> Mechanical properties of the vinyl chloride systems will now be considered in the light of the observed  $T_g$  behavior.

#### Correlation of the Mechanical Properties with Composition for the Vinyl Chloride Systems

Insert A of Figure 6 compares torsional modulus at room temperature, 23°C, with the weight fraction of, respectively, allyl stearate, vinyl stearate,

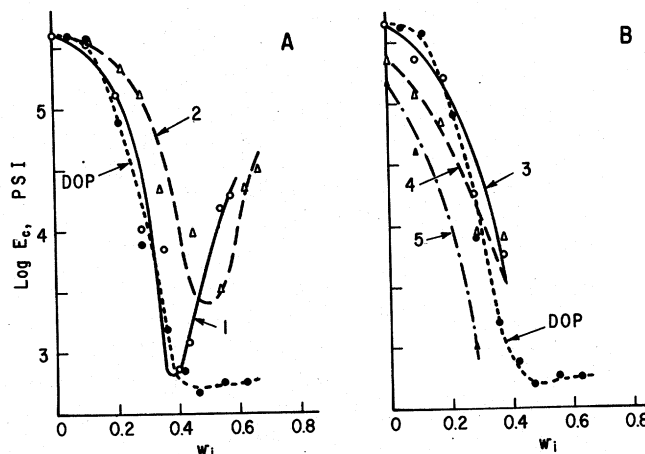


Fig. 6. Plot of torsional modulus at room temperature (23°C)  $E_c$  vs. the weight fraction of plasticizer  $w_i$  in the polymer: (1) copolymers of allyl stearate and vinyl chloride; (2) copolymers of vinyl stearate and vinyl chloride; (3, 4, 5) terpolymers of allyl stearate, vinyl acetate, and vinyl chloride, having vinyl chloride feed compositions of, respectively, 0.60, 0.40, 0.20 mole fraction. Data for mixtures of di-2-ethylhexyl phthalate (DOP) and poly(vinyl chloride) are shown in both inserts for comparison (dotted line).

and di-2-ethylhexyl phthalate (DOP). Data for the last system came from another study in this laboratory.<sup>24</sup> Softer compositions were produced by allyl stearate than by vinyl stearate for the same weight fraction of comonomer. In fact, the efficiency of modulus reduction compared with that produced by DOP. However, side-chain crystallinity development in the internal systems (evidenced by rising moduli) limited the soft region to a narrow range of composition, compared to the externally plasticized compositions. When vinyl acetate was present as a third component (Fig. 6, insert *B*), even greater efficiency was realized (curves 4 and 5) in reducing moduli compared to DOP. However, (Fig. 7, insert *A*) tensile

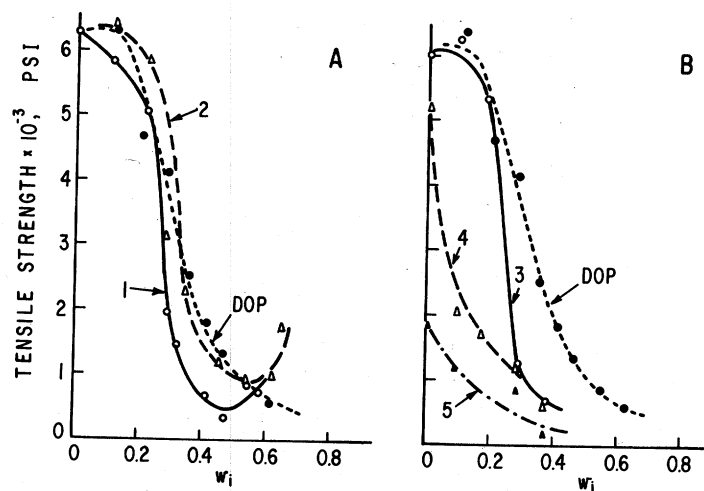


Fig. 7. Plot of tensile strengths at room temperature (23°C) vs. the weight fraction of plasticizer  $w_i$  in the polymers: (1) copolymers of allyl stearate and vinyl chloride; (2) copolymers of vinyl stearate and vinyl chloride; (3, 4, 5) terpolymers of allyl stearate, vinyl acetate, and vinyl chloride, having a vinyl chloride feed composition of, respectively, 0.60, 0.40, 0.20 mole fraction. Data for mixtures of di-2-ethylhexyl phthalate (DOP) are shown in both inserts for comparison (dotted line).

strengths were reduced considerably more for any given weight fraction of allyl stearate than by either DOP or vinyl stearate. Again, the diluent mixture had the best ultimate properties and greatest elongations (Table II)<sup>16</sup> at all weight fractions. The tensile properties of the terpolymers (Fig. 7, insert *B*) were clearly inferior to all other systems investigated. The tensile behavior observed in this study illustrates the effect of the reduction in relaxation times associated with loss of chain entanglements as molecular weight decreases.<sup>23</sup> Imperfect networks in soft polymers lead to premature failure.<sup>42</sup> While the network introduced by side-chain crystallinity did raise tensile strength slightly (Fig. 7, insert *A*), elongations were sharply reduced (Table II). Aggregations of side chains in crystals probably act as stress concentrators<sup>43</sup> and prevent the attainment of high tensile strengths.<sup>15, 16</sup>

Isochronal modulus-temperature curves for representative allyl stearate and vinyl stearate copolymers with vinyl chloride are compared in Figure 8. Comparisons are made at the same feed composition, although the found compositions (Table I) are actually somewhat different. Moduli for the allylic copolymers were shifted slightly to lower temperatures, even though these copolymer compositions had less plasticizer than their vinyl ester counterparts. This again reflects the slightly greater efficiency of allyl stearate in reducing moduli discussed above. The development of side-chain crystallinity (Fig. 9) distorted the curves more than those in Figure 8

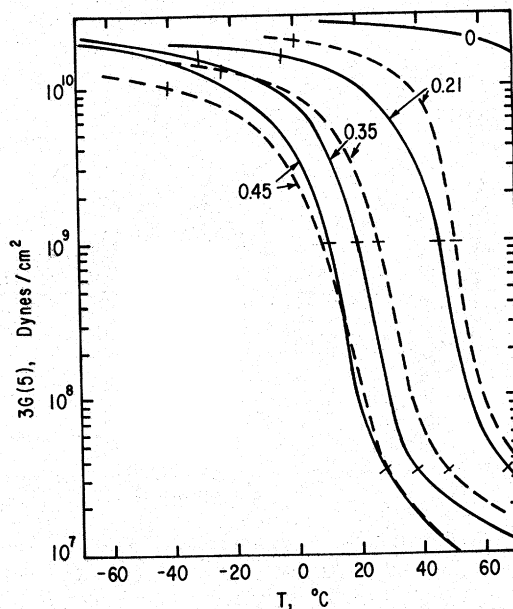


Fig. 8. Torsional moduli vs. temperature for selected amorphous copolymers of vinyl chloride: (—) allyl stearate copolymers; (---) vinyl stearate copolymers. Numbers are the weight fraction of fatty ester in the feed (Table I).

for both the allyl stearate copolymers (solid lines) and the vinyl stearate copolymers (dashed lines) and shifted them to higher temperatures. This effect has been extensively discussed elsewhere.<sup>24</sup> Again the allyl ester copolymers were shifted to lower temperatures than the vinyl ester copolymers, even though the extents of crystallinity<sup>19,24</sup> for the two systems (Table II) were essentially the same.

It may be concluded, from these limited data, that replacement of vinyl stearate by allyl stearate in copolymers with vinyl chloride results in modulus reductions of the same magnitude with respect to both temperature and composition, although the allyl ester seems to be somewhat more efficient. This small advantage is more than offset by a more rapid tensile reduction with the allylic comonomers. Differences in entanglement coupling seemed responsible for the observed behavior.

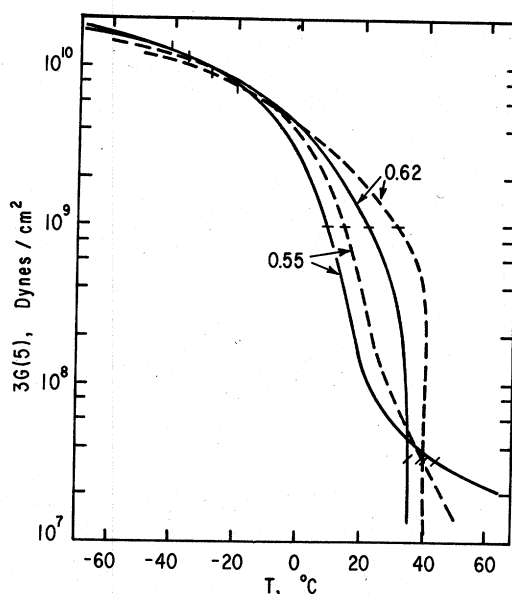


Fig. 9. Torsional moduli vs. temperature for selected copolymers of vinyl chloride exhibiting side-chain crystallinity: (—) allyl stearate copolymers; (---) designate vinyl stearate copolymers. Numbers are the weight fraction of fatty ester in the feed (Table I).

All of the isochronal-temperature data collected for the allyl and vinyl stearate systems of Tables I and II are summarized in Table IV, in the form of arbitrary, but convenient, parameters. These were defined and discussed in a previous publication.<sup>24</sup> Moduli are again expressed as dynes/cm<sup>2</sup> to permit ready comparison with literature values.<sup>44-48</sup> Designations of the parameters<sup>24</sup> of Table IV are summarized below. The approximate inflection temperature at  $10^9$  dynes/cm<sup>2</sup> is  $T_i$  and  $s$  is its slope. Moduli  $3G_1$  and  $3G_2$  were taken, respectively, 50°C below and above the inflection temperature  $T_i$ , and  $s_1$  is the slope at  $3G_1$ . The temperature where the modulus declined to  $3.45 \times 10^7$  dynes/cm<sup>2</sup> ( $T_{3.45}$ ) is designated the modulus of a soft polymer of generally useful strength. The rate of change of modulus with temperature in this region ( $s_2$ ), taken together with the difference  $T_{3.45} - T_i$ , ( $\Delta T$ ), give a rough index of the use temperature range; the higher  $\Delta T$  and the lower  $s_2$  the more useful a composition will be. By using the parameters  $3G_1$ ,  $s_1$ ,  $s$ ,  $s_2$ , and  $T_i$ , estimates of the original Clash Berg curves can be constructed for each experiment in the table.

Only slight differences were again found in the parameters of the allyl stearate and vinyl stearate copolymers. This parallels behavior just seen graphically for selected copolymers in Figures 8 and 9. The use-temperature index  $\Delta T$  and slope  $s_2$  were similar for both classes. Glassy moduli  $3G_1$  were again found to decline with increase in allyl or vinyl ester content.<sup>24</sup> This effect had previously been tentatively attributed to subgroup motions in side chains, leading to lowered moduli, compared to vinyl chloride

TABLE IV  
Viscoelastic Parameters from the Modulus-Temperature Curves

Expt. no. <sup>a</sup>	$w_b$ , found	$T_g$ , °C	$T_i$ , °C	$-\delta$	$3G_1$ $\times 10^{-10}$ , dynes/cm <sup>2</sup>	$-\delta_1$	$3G_2$ $\times 10^{-7}$ , dynes/cm <sup>2</sup>	$T_{3.45}$ , °C <sup>b</sup>	$-\delta_2^c$	$\Delta T$ , °C <sup>d</sup>
Copolymers: allyl stearate and vinyl chloride										
13	0	80.9	89.5	0.14	2.4	0.0017	6.0	174.0	0.0041	84.5
14	0.111	56.9	63.8	0.13	2.3	0.0015	2.90	89.0	0.013	25.2
15	0.209	31.9	46.0	0.084	1.6	0.0049	1.72 <sup>e</sup>	67.0	0.022	21.0
16	0.287	23.9	23.5	0.071	1.7	0.0082	1.65 <sup>e</sup>	52.0	0.020	28.5
17	0.319	16.9	19.5	0.078	1.5	0.0043	1.12 <sup>e</sup>	38.0	0.027	18.5
18	0.402	4.9	10.0	0.013	1.5	0.0131	0.69 <sup>e</sup>	27.0	0.032	17.0
19	0.469	19.9	8.0	0.060	0.53	0.0055	2.3 <sup>e</sup>	44.0	0.014	36.0
20	0.544	20.9	21.0	0.031	0.97	0.0089	—	35.0	1.75	14.0
21	0.579	21.9	27.5	0.029	0.93	0.0075	—	34.0	$\infty$	6.8
Copolymers: vinyl stearate and vinyl chloride										
22	0.119	58.9	66.4	0.084	2.5	0.0024	3.2	110.0	0.0054	43.6
23	0.225	40.9	50.0	0.12	2.0	0.013	2.6	74.0	0.011	24.0
24	0.286	24.9	40.0	0.12	1.7	0.0039	1.3 <sup>e</sup>	54.0	0.025	14.0
25	0.348	12.9	26.2	0.086	1.3	0.0051	1.9 <sup>e</sup>	43.5	0.025	17.3
26	0.455	1.9	9.7	0.053	1.0	0.0011	0.83 <sup>e</sup>	27.5	0.041	17.8
27	0.543	16.9	13.5	0.056	1.1	0.0077	0.48 <sup>e</sup>	39.0	0.044	25.5
28	0.623	18.9	30.0	0.027	0.76	0.0089	—	40.0	2.0	10.0
29	0.659	18.9	35.5	0.038	0.76	0.0075	—	40.0	2.8	4.5



Terpolymers: allyl stearate, vinyl stearate, and vinyl chloride

30	0.113	57.0	60.0	0.093	2.4	0.0013	2.75	95.0	0.010	35.0
31	0.204	27.0	42.0	0.096	1.9	0.0024	2.34	65.0	0.022	23.0
32	0.290	24.0	25.5	0.076	1.5	0.0071	1.65 <sup>c</sup>	48.5	0.031	23.0
33	0.340	18.0	24.0	0.089	1.2	0.0049	1.72 <sup>c</sup>	41.0	0.053	17.0
34	0.416	9.0	11.5	0.071	1.2	0.0048	0.862 <sup>c</sup>	28.0	0.070	16.5
35	0.498	17.0	10.0	0.064	1.3	0.0080	—	34.0	0.102	24.0
36	0.583	7.0	25.0	0.030	0.83	0.0087	—	39.7	0.081	14.7
37	0.662	18.0	21.0	0.030	0.63	0.0049	—	37.0	0.036	16.0

<sup>a</sup> Experiment numbers correspond to those in Table I and II.

<sup>b</sup> Temperature at which the modulus was  $3.45 \times 10^7$  dynes/cm<sup>2</sup> or 500 psi.

<sup>c</sup> Slope at  $T_{3.45}$ .

<sup>d</sup>  $\Delta T = T_{3.45} - T_i$ .

<sup>e</sup> Estimated by a short extrapolation; data very approximate.

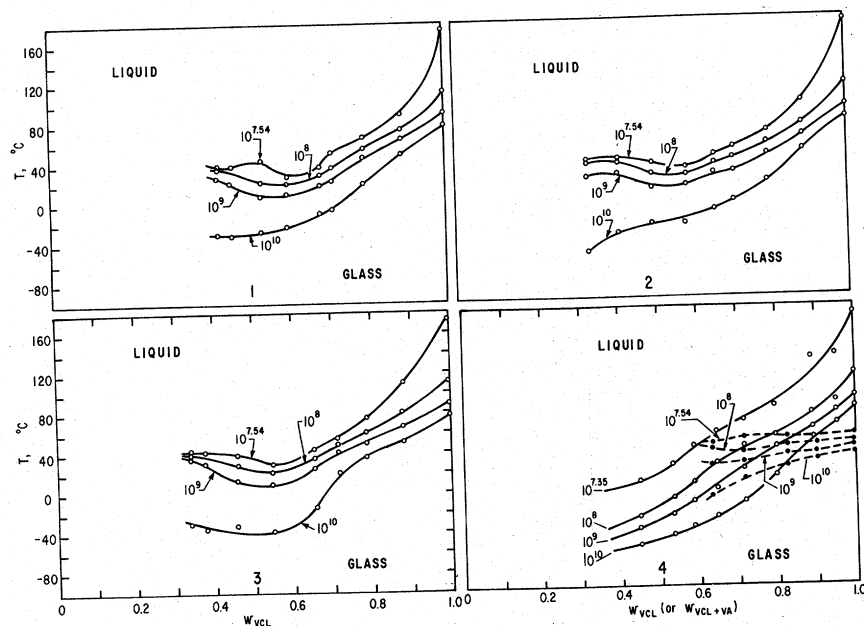


Fig. 10. Isochronal temperature-composition diagrams for mixtures and for selected copolymers and terpolymers: (1) copolymers of allyl stearate and vinyl chloride; (2) terpolymers of allyl stearate, vinyl stearate, and vinyl chloride; (3) copolymers of vinyl stearate and vinyl chloride; (4) mixtures of poly(vinyl chloride) and di-2-ethylhexyl phthalate (DOP) (—) and terpolymers of allyl stearate, vinyl acetate, and vinyl chloride containing 0.40 mole fraction of vinyl chloride (---).

plasticized by DOP, where  $3G_1$  declined only slightly.<sup>24</sup> No special property advantage was found by incorporating vinyl stearate in terpolymers with allyl stearate; mechanical properties generally lay between the two copolymer systems, any difference being trivial.

Correlation of selected viscoelastic data of this paper, with both temperature and composition, is shown graphically in Figure 10. Diagrams of this type, attributable to Yannas,<sup>49</sup> were described in a previous publication.<sup>24</sup> In Figure 10, insert 1 is torsional moduli data for copolymers of allyl stearate and vinyl chloride; insert 2, terpolymers of allyl stearate, vinyl stearate, and vinyl chloride; insert 3, copolymers of vinyl stearate and vinyl chloride; and insert 4, mixtures of di-2-ethylhexyl phthalate (DOP) and vinyl chloride. The solid lines and dashed line in insert 4 (isothernes) are readings taken at the indicated moduli in dynes/cm<sup>2</sup>. Vertical readings (isopleths) are the modulus-temperature curves discussed at specific compositions in Figures 8 and 9; horizontal readings (isotherms) give data for moduli as a function of composition (Fig. 6). The area below the isothene 10<sup>10</sup> dynes/cm<sup>2</sup> in the figure is designated the glassy region; that considerably above 10<sup>7.54</sup> dynes/cm<sup>2</sup>, the terminal region<sup>23</sup> of steady-state viscosity. Data defining the rubbery plateau were not available, but this region lies immediately above the isothene 10<sup>7.54</sup>. The diagrams in inserts 1, 2, and 3 are very similar, differing only in details. These

illustrate features apparently common<sup>15,16,24,28</sup> to many systems internally plasticized by comonomers having side chains long enough to crystallize.<sup>14,18-21,24,28</sup> The shift of modulus to lower temperatures is interrupted by developing side-chain crystallinity, which occurs at a plasticizer weight fraction of about 0.4-0.6. In this composition region the isotherms go through a minimum, then move up the temperature scale and thereby oppose plasticization. The diagrams for mixtures containing DOP (insert 4) are in striking contrast. Plasticization efficiency is greater (magnitude of the derivatives of the isotherms), the isopleths broader, and all moduli lie much lower than the room temperature isotherm than can the internally plasticized systems. The dashed line in insert 4 illustrates the generally limited properties conferred by incorporating vinyl acetate, as was discussed in the sections above.

### Effect of Side-Chain Crystallinity

The heat of fusion for poly(allyl stearate) was (expt. 1, Table II) 7692 cal/mole; this value compares with a value of 6154 cal/mole for poly(vinyl stearate)<sup>18</sup> or 6925 cal/mole for poly(*n*-octadecyl acrylate),<sup>18</sup> which is isomeric with the poly(allyl ester). If it is assumed that only side-chain methylenes are crystalline and there is little perturbation from packing the ends of crystallites, the increase in enthalpy for poly(allyl stearate) is equivalent to an increase of two methylene groups over poly(vinyl stearate) and one over the acrylate ester, providing the crystal form remains hexagonal.<sup>18,20,21</sup> Recent information indicates that the main-chain units of linearly branched polyesters are in crystallites, and the total length of the side chains are packed in the hexagonal modification.<sup>20,21</sup> This requirement would reduce the internal energy to accommodate the packing of bulky and strained groups.<sup>50</sup> More thermal and x-ray data on homologs are obviously needed to describe the solid state of poly(allyl esters). However, the similarity of the heat of fusion for poly(allyl stearate) to the values for other fatty homopolymers<sup>18</sup> does suggest that oligomerization does not appreciably alter the overall picture. Monomers, including allyl stearate (15,392 cal/mole), have much higher values, even when the polymorph is hexagonal.<sup>50</sup>

Heats of fusion and melting points are illustrated in Figure 11 for copolymers of allyl and vinyl stearate and for allyl stearate and vinyl chloride. The linear relation between the melting points and the mole fraction of allyl stearate is clear evidence that isomorphism characterizes the melting behavior. This had been observed previously for other copolymers and mixtures of long-chain homopolymers having similar side-chain lengths.<sup>18,51</sup> It was taken as convincing evidence that only side chains are in the crystal lattice. The linear relation of the heat of fusion for the allyl and vinyl stearate copolymers also indicates that the extent of crystallinity was not reduced as allyl stearate replaced the vinyl ester in the copolymers. Packing of both structures in the same lattice could lead to the maximum attainable crystallinity<sup>19</sup> and the linear relation observed.

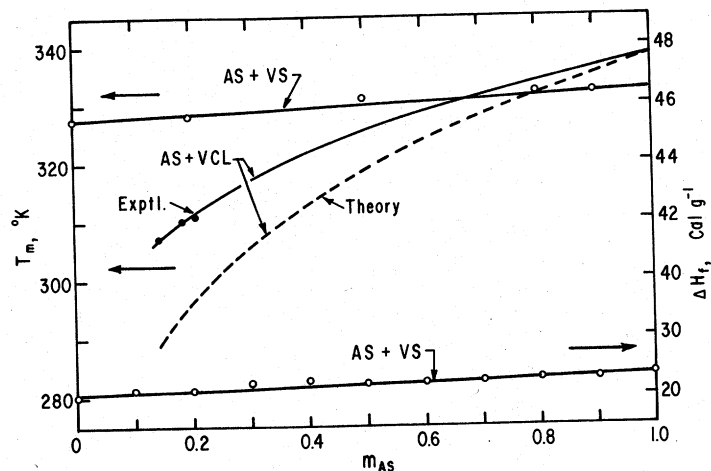


Fig. 11. Plots of the melting point  $T_m$  and heats of fusion  $\Delta H_f$  vs. the mole fraction of allyl stearate  $m_{AS}$  in copolymers of allyl stearate, (AS) and vinyl chloride (VS) and copolymers of allyl stearate and vinyl chloride (VCL). The experimental line for the allyl stearate-vinyl chloride copolymers as computed by using eq. (15) but experimental melting points; the theoretical line was obtained by using the observed  $\Delta H_f$  for poly(allyl stearate), 7692 cal/mole, in the same equation. Melting points for the vinyl stearate copolymers were obtained by using a refractometer; those for the vinyl chloride copolymers were obtained by differential scanning calorimetry.

In contrast, depression of melting point was found for the copolymers of allyl stearate and vinyl chloride. Here the vinyl chloride acts as an amorphous component.<sup>19</sup> Depression was less than that predicted by theory, by use of the relation of Flory<sup>52</sup>

$$1/T_m - 1/T_{m0} = (-R/\Delta H_f) \ln m_{AS} \quad (15)$$

where  $T_m$  is the equilibrium melting point,  $T_{m0}$  the corresponding melting point of the homopolymer,  $\Delta H_f$  the apparent heat of fusion of the crystalline phase, and  $m_{AS}$  the mole fraction of allyl stearate. This is shown as the dashed line in the figure and was computed by using  $\Delta H_f$  of the homopolymer, 7692 cal/mole. The solid line was also computed by using eq. (15), but after using the experimental melting points (Table II) to calculate the apparent  $\Delta H_f$ .<sup>19</sup> The displacement at  $m_{AS} = 1.0$  is the result of using differential scanning calorimetry to obtain these data; the other melting points in the figure are by refractometry. Consequently, melting point depression was less than theory for these copolymers. This had been observed for other copolymers of amorphous comonomers with *n*-octadecyl acrylate.<sup>19</sup> The moderation was attributed to the formation of larger crystallites than specified by the segmental distribution,<sup>19</sup> because opportunities exist for overlapping of many of the side chains. The behavior of allyl stearate in copolymers also seems to be insensitive to its degradative nature.

## Summary

The homopolymer, poly(allyl stearate), and copolymers of this monomer with vinyl chloride, together with terpolymers, containing vinyl chloride and allyl stearate further modified by vinyl stearate or vinyl acetate, were studied over a wide range of composition. Areas investigated included reduction in molecular weight and conversion by degradative chain transfer, the glass transition of amorphous systems, comparison of mechanical properties of vinyl chloride containing compositions, and determination of limited thermodynamic data on the crystallinity present in side chains. The lowering of molecular weight in copolymers was correlated with the segmental concentration of the allyl groups in the chain. The glass transition was unaffected by lowered molecular weight in these systems, in which side chains dominate the reduction. In contrast, mechanical properties, particularly tensile strength, of the vinyl chloride systems were more reduced than those of their vinyl stearate counterparts. Side-chain crystallinity behavior resembled that of more typical vinyl polymers.

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Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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